

Atmospheric Deposition of Sulfur and Nitrogen Compounds

<http://www.epa.gov/oar/aqtrnd99/chapter7.pdf>

Worth Noting:

- 1990's improvements in wet sulfur deposition, rural ambient SO₂, and rural ambient sulfates followed the large reductions in regional emissions in SO₂. Most of the emissions and reductions come from power plants.
 - 10-year changes in the eastern United States: annual average sulfates, -24 percent; annual average SO₂, -32 percent; regional power plant emissions, -25 percent.
 - 2-year changes in the eastern United States: (1998–99): annual average sulfates, -10 percent; annual average SO₂, -4 percent; regional power plant emissions, -6 percent.
- The largest sulfate improvements occur during the third calendar quarter.
 - 10-year changes: quarterly average sulfates, -33 percent.
 - 2-year changes (1998–99): quarterly average sulfates, -17 percent.
- These regional reductions in particle sulfates benefit visibility and PM_{2.5} levels.

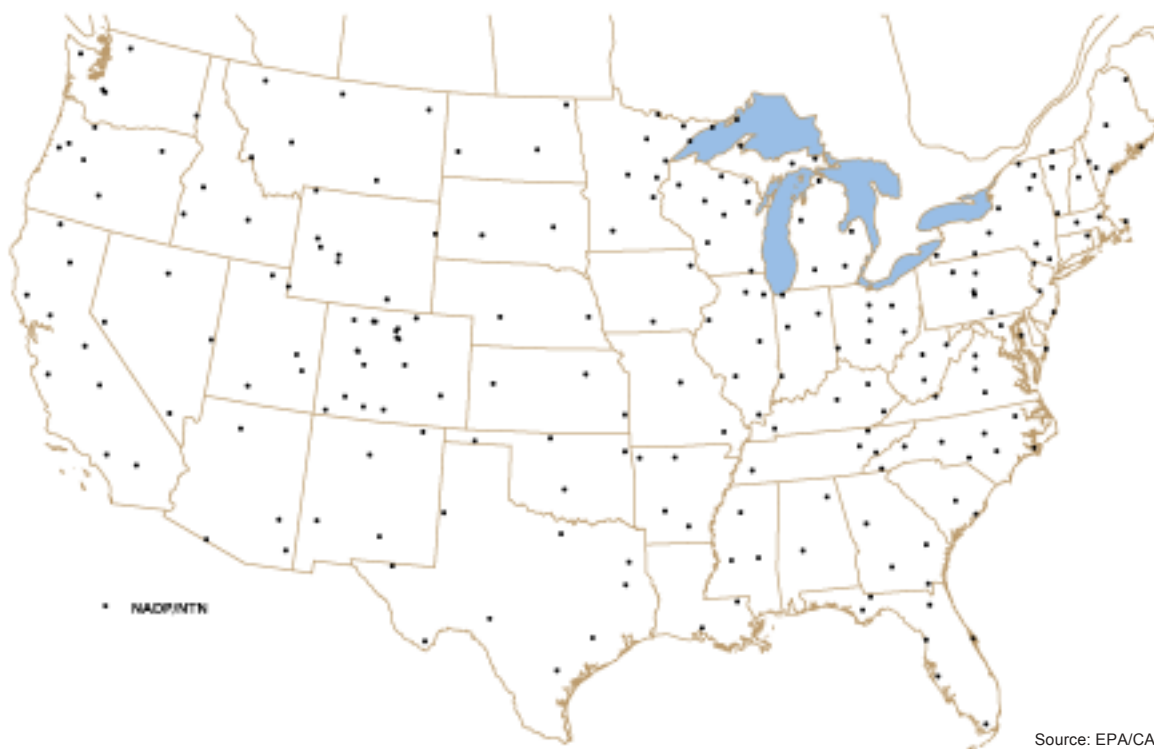
Sulfur and nitrogen oxides are emitted into the atmosphere primarily from the burning of fossil fuels. These emissions react in the atmosphere to form compounds that are transported long distances and are subsequently deposited in the form of pollutants such as particulate matter (sulfates, nitrates) and related gases (nitrogen dioxide, sulfur dioxide and nitric acid). Nitrogen oxides also will interact with volatile organic compounds to form ozone. The effects of atmospheric deposition include acidification of lakes and streams, nutrient enrichment of coastal waters and large river basins, soil nutrient depletion and decline of sensitive forests, agricultural crop damage, and impacts on ecosystem biodiversity. Toxic pollutants and metals also can be transported and deposited through atmospheric processes. (See Chapter 5: Air Toxics.)

Both local and long-range emission sources contribute to atmospheric deposition. Total atmospheric deposition is determined using both wet and dry deposition measurements. Wet deposition is the portion dissolved in cloud droplets and is deposited during rain or other forms of precipitation. Dry deposition includes both gas and particle transfer

to surfaces during periods of no precipitation. Although the term “acid rain” is widely recognized, the dry deposition portion can range from 20–60 percent of total deposition.

EPA is required by several Congressional and other mandates to assess the effectiveness of air pollution control efforts. These mandates include Title IX of the Clean Air Act Amendments (the National Acid Precipitation Assessment Program), the Government Performance and Results Act, and the U.S./Canada Air Quality Agreement. One measure of effectiveness of these efforts is whether sustained reductions in the amount of atmospheric deposition over broad geographic regions are occurring. However, changes in the atmosphere happen very slowly and trends are often obscured by the wide variability of measurements and climate. Numerous years of continuous and consistent data are required to overcome this variability, making long-term monitoring networks especially critical for characterizing deposition levels and identifying relationships among emissions, atmospheric loadings and effects on human health and the environment.

For wet and dry deposition, these studies typically include measure-

Figure 7-1. The National Atmospheric Deposition Program/National Trends Network.

Source: EPA/CAMD 04/04/01

ment of concentration levels of key chemical components as well as precipitation amounts. For dry deposition, analyses also must include meteorological measurements that are used to estimate rate of the actual deposition, or “flux.” Data representing total deposition loadings (e.g., total sulfate or nitrate) are what many environmental scientists use for integrated ecological assessments.

Primary Atmospheric Deposition Monitoring Networks

The National Atmospheric Deposition Program/National Trends Network (NADP/NTN) and the Clean Air Status and Trends Network (CASTNet) were developed to monitor wet and dry acid deposition, respectively. Monitoring site locations are predominantly rural by

design to assess the relationship between regional pollution and changes in regional patterns in deposition. CASTNet also includes measurements of rural ozone and the chemical constituents of $PM_{2.5}$. Rural monitoring sites of NADP/NTN and CASTNet provide data where sensitive ecosystems are located and provide insight into natural background levels of pollutants where urban influences are minimal. Scientists and policy analysts use these data to evaluate environmental effects, particularly those caused by regional sources of emissions for which long-range transport plays an important role. Measurements from these networks also are important for understanding non-ecological impacts of air pollution such as visibility impairment and damage to materials, particularly those of cultural and historical importance.

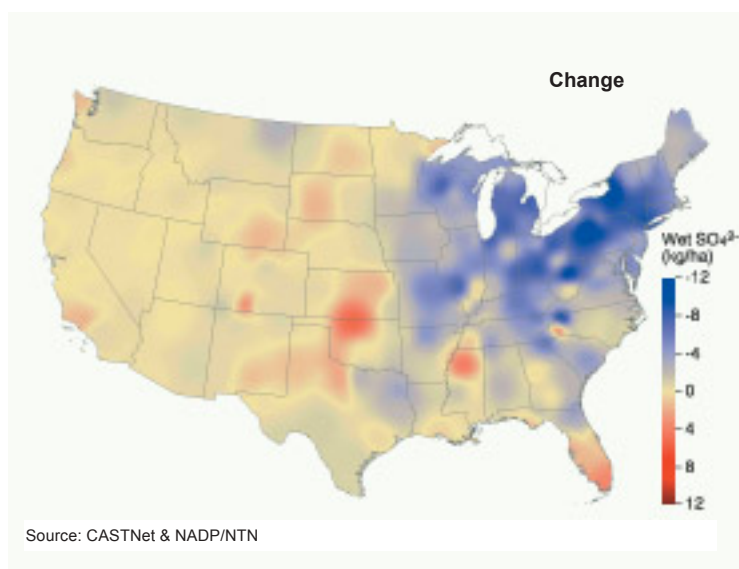
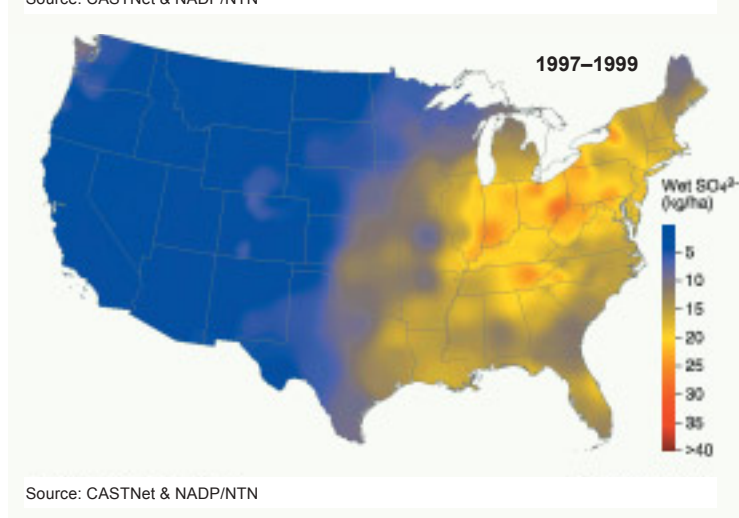
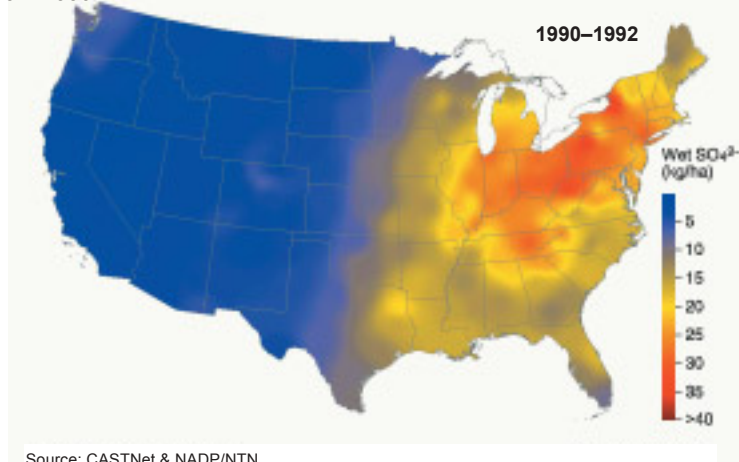
They also provide important information to support the NAAQS.

National Atmospheric Deposition Network/National Trends Network

The National Atmospheric Deposition Program/National Trends Network is a cooperative program between federal and state agencies, universities, electric utilities and other industries that has measured precipitation chemistry in the United States since 1978. As one of the world’s largest and longest running deposition monitoring networks, it is composed of over 200 sites and is able to determine geographic patterns and trends in precipitation chemistry (see Figure 7-1).

The NADP/NTN analyzes the constituents important in precipitation chemistry, including those affecting rainfall acidity and those that

Figure 7-2. Annual mean sulfate deposition from precipitation, 1990–1992 vs. 1997–1999.



may have ecological effects. The Network measures sulfate, nitrate, hydrogen ion (measure of acidity), ammonia, chloride, and base cations (calcium, magnesium, potassium). To ensure comparability of results, laboratory analyses for all samples are conducted by NADP's Central Analytical Lab at the Illinois State Water Survey. A new subnetwork of the NADP, the Mercury Deposition Network (MDN) measures mercury in precipitation. For more information on the MDN, see Chapter 5: Air Toxics.

Trends Analyses for Sulfate and Nitrogen Concentrations in Wet Deposition

Sulfate concentrations in precipitation have decreased over the past two decades.¹ The reductions were relatively large in the early 1980s followed by more moderate declines until 1995. These reductions in wet sulfates are similar to changes in SO_2 emissions. In 1995 and 1996, however, concentrations of sulfates in precipitation over a large area of the eastern United States exhibited a dramatic and unprecedented reduction. Sulfates in rain have been estimated to be 10–25 percent lower than levels expected with a continuation of 1983–1994 trends.² The wet sulfate deposition levels in the 1990–1992 and 1997–1999 time periods, together with the absolute change are illustrated in Figure 7-2. This important reduction in acid precipitation is directly related to the large regional decreases in SO_2 emissions resulting from phase I of the Acid Rain Program (see “Trends in SO_2 ” in Chapter 2 of this report). The largest reductions in wet sulfate deposition occurred along the Ohio River Valley

and in states to the north and immediately downwind of this region. Nitrogen trends paint a different picture. Nitrate and ammonium deposition derived from NADP/NTN measurement sites reveal 10-year improvement in some areas, including eastern TX, MI, PA and NY. Increased deposition is estimated for the Plains States; and the western Ohio River and Central Mississippi River Valleys. From ammonium in rain, increases are also noted for eastern NC. However, most areas of the country were not appreciably different in either oxidized or reduced 1997–1999 nitrogen from historical levels (see Figures 7-3 and 7-4).

Clean Air Status and Trends Network

The Clean Air Status and Trends Network provides atmospheric data on the dry deposition component of total acid deposition, ground-level ozone and other forms of atmospheric pollution. CASTNet is considered the nation's primary source for atmospheric data to estimate dry acidic deposition and to provide data on rural ozone levels. Used in conjunction with other national monitoring networks, CASTNet is used to determine the effectiveness of national emission control programs. Established in 1987, CASTNet now comprises 79 monitoring stations across the United States. The longest data records are primarily at eastern sites. The majority of the monitoring stations are operated by EPA's Office of Air and Radiation; however, 27 stations are operated by the National Park Service (NPS) in cooperation with EPA. Of the total number of sites, 74 measure dry-deposition, 68 measure ozone, and eight measure aerosols for visibility assessment.

Figure 7-3. Annual mean ammonium deposition from precipitation, 1990–1992 vs. 1997–1999.

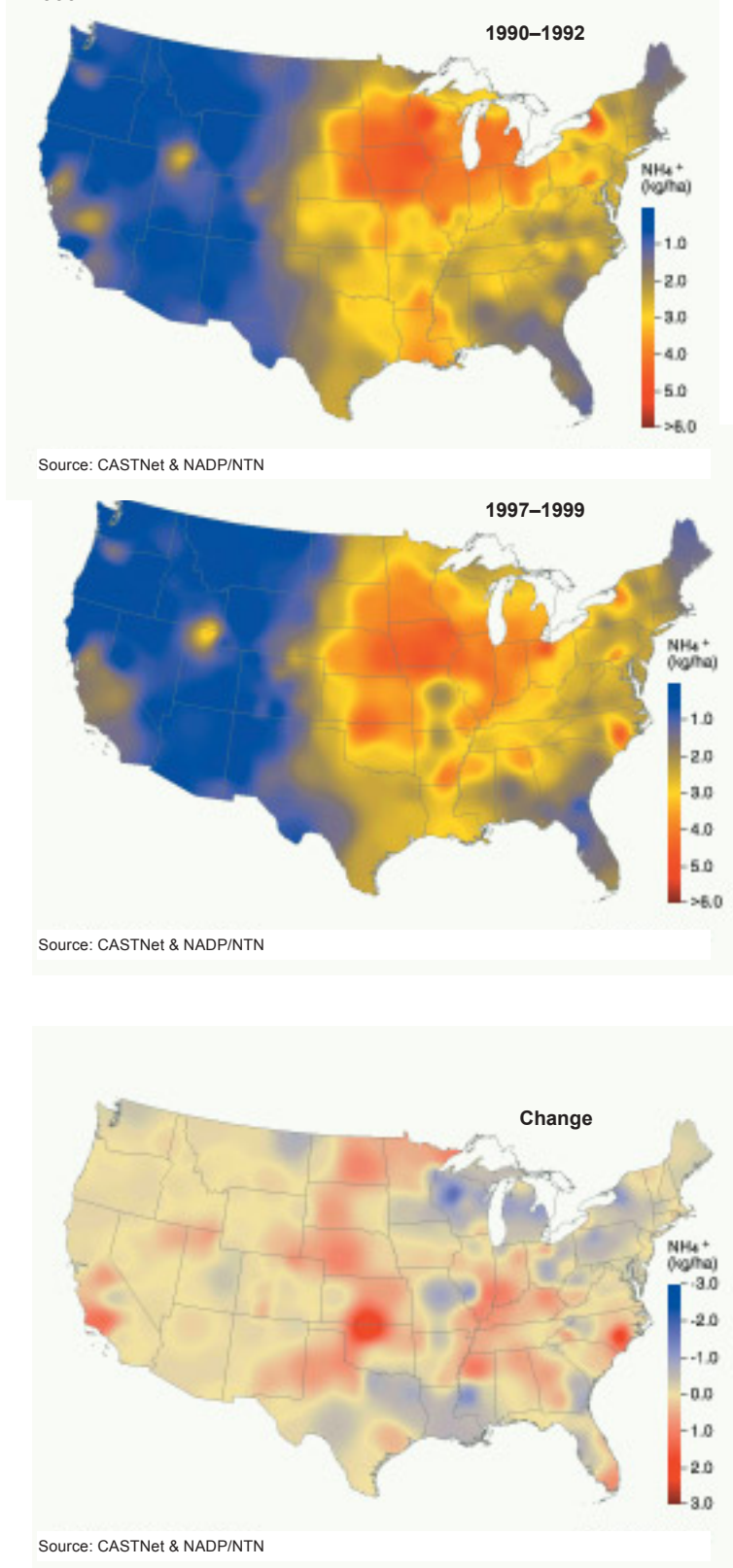
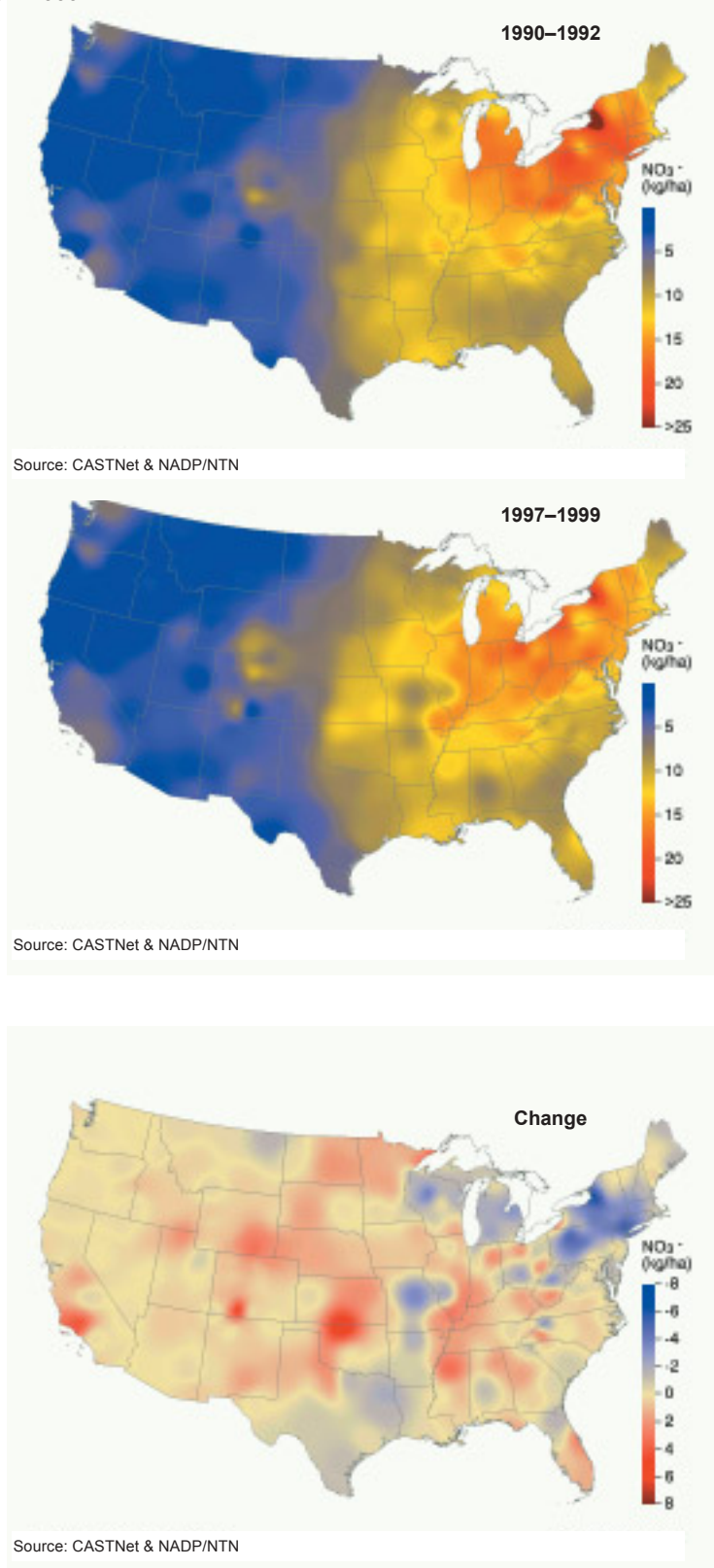


Figure 7-4. Annual mean nitrate deposition from precipitation, 1990–1992 vs. 1997–1999.



Each CASTNet dry deposition station measures:

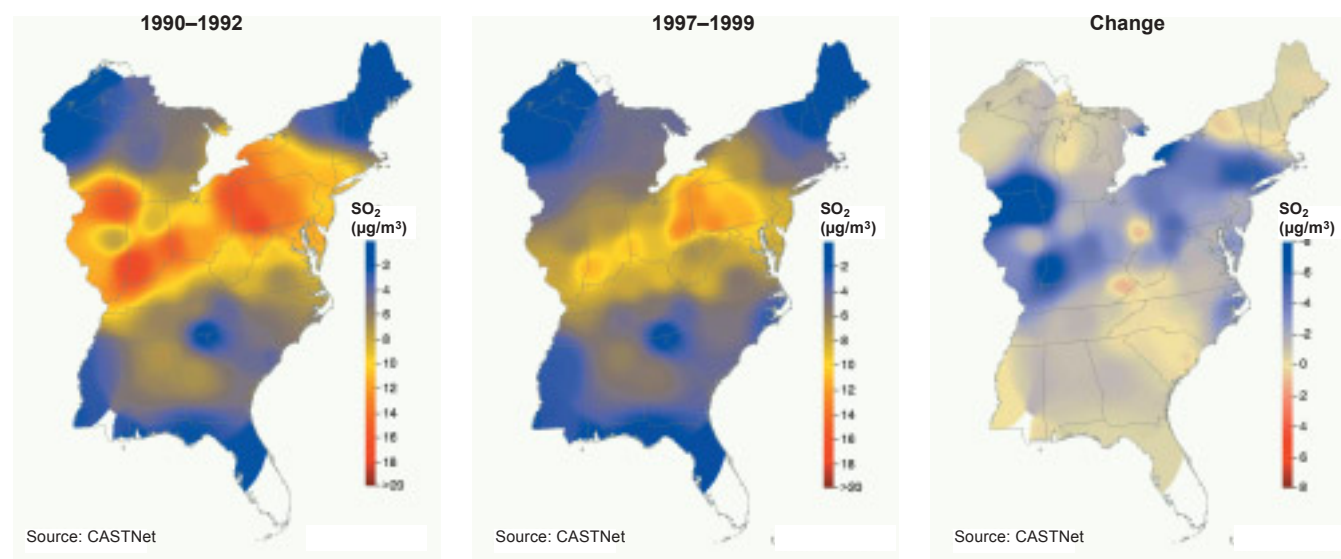
- Weekly average atmospheric concentrations of sulfate, nitrate, ammonium, sulfur dioxide, and nitric acid (sulfate, nitrate and ammonium generally exist as fine particles).
- Hourly concentrations of ambient ozone levels.
- Meteorological conditions required for calculating dry deposition rates.

Dry Deposition

Dry deposition rates are calculated using atmospheric concentrations, meteorological data and information on land use, vegetation, and surface conditions. CASTNet complements the database compiled by NADP/NTN. Together, these two long-term databases provide the necessary data to estimate trends and spatial patterns in total atmospheric deposition. NOAA also operates a smaller dry deposition network called Atmospheric Integrated Assessment Monitoring Network (AIRMoN) focused on addressing research issues specifically related to dry deposition measurement.

Concentration Trends Analysis at CASTNet Sites

CASTNet ambient concentration data in the eastern United States were analyzed for the period 1990–1999 for the change in ambient sulfur dioxide, sulfates, total nitrates and ammonium. First, maps are presented for a comparison of 3-year periods at the beginning and end of the 10-year period based on data from all 51 eastern locations in the CASTNet monitoring program. Then data from a subset of 34 eastern CASTNet sites with the most complete historical record are examined for year to year changes from 1990–1999.³

Figure 7-5. Rural annual mean SO₂ concentrations from CASTNet, 1990–1992 vs. 1997–1999.

In the early 1990s, ambient SO₂ concentrations in the rural eastern United States were highest in western Pennsylvania, along the Ohio Valley and in the vicinity of Chicago/Gary Indiana. Large improvement in ambient SO₂ air quality can be seen in Figure 7-5 by comparing 1990–1992 with 1997–1999. The largest decreases in concentrations are noted in the vicinity of Chicago and throughout the states bordering the Ohio Valley (IL, IN, OH, PA, KY, WV). The highest SO₂ concentrations in the rural parts of the eastern United States are now concentrated in southwestern PA.

Figure 7-6 shows that sulfate concentrations greater than 5 µg/m³* cover most of the eastern United

*Sulfate concentrations represent the sulfate ion, SO₄²⁻, and do not represent the compounds (i.e., ammonium sulfate or ammonium bisulfate) typically associated with this analyte.

States in the 1990–1992 period. Regions of concentrations greater than 6 µg/m³ are estimated to cover the Ohio Valley States (IL, IN, OH, KY, WV), Pennsylvania, and the other mid-Atlantic states from New Jersey to Virginia. The highest sulfate concentrations (> 7 µg/m³) were adjacent to the Ohio Valley and in northern Alabama. These are the locations of large electric utilities.

During the late 1990s, ambient average sulfates lowered dramatically. Although there are differences in the measured concentrations among these individual years, both the size of the region with high concentrations as well as the magnitude of those concentrations have decreased.

Based on 34 CASTNet sites with 10 years of measurement data (Figure 7-7), mean rural sulfur dioxide concentrations were reduced by 32 percent and mean rural sulfate levels

were reduced by 24 percent. The regional distribution of annual average concentrations is presented as box-plots in Figures 7-8 and 7-9. A 10-percent decrease in mean sulfates and 4-percent decrease in annual mean sulfur dioxide between 1998 and 1999 is also noted. This is a reversal of the 2-year increase previously reported for 1997–1998.

Levels and spatial changes in ambient nitrates in the rural east are shown in Figure 7-10. No significant change is noted in total nitrate concentrations. The trend in average total nitrate concentrations (nitrates plus nitric acid) among the 34 trend sites was level, corresponding to the small change in NO_x emissions during this period. The stable regional average nitrate trend line is not shown. The highest nitrate concentrations in the East are recorded in Ohio, Indiana, and Illinois. As shown in

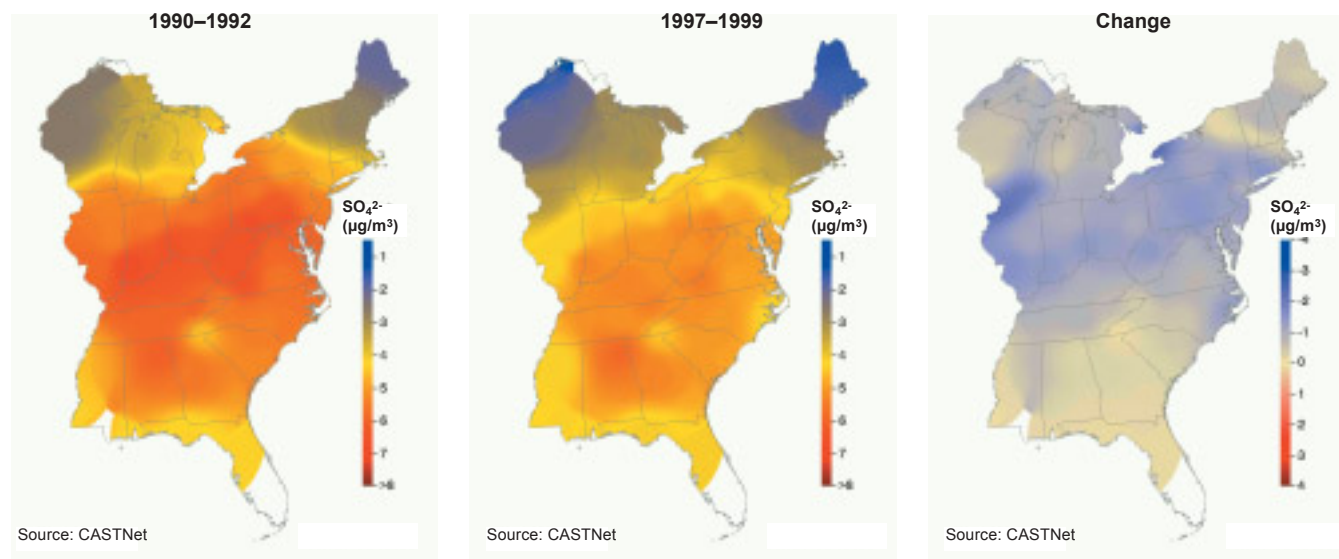
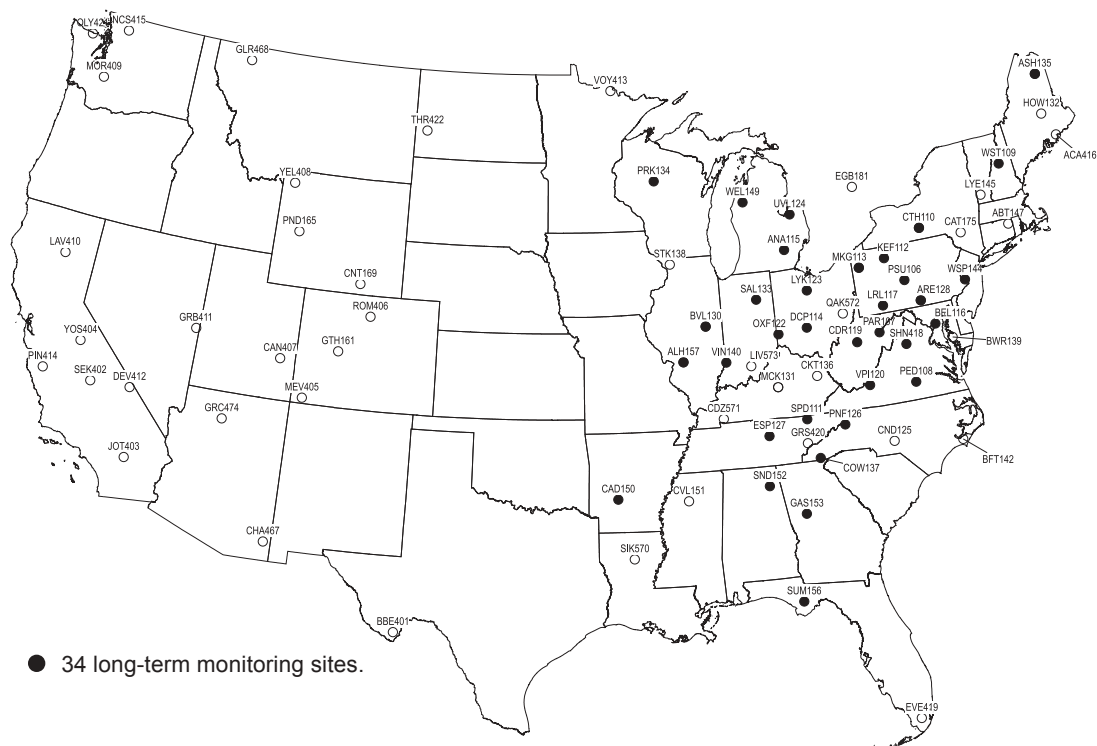
Figure 7-6. Rural annual average sulfate concentrations from CASTNet, 1990–1992 vs. 1997–1999.**Figure 7-7.** CASTNet and subset of 34 long-term monitoring sites used for 1990–1999 trends analysis.

Figure 7-10, the 10-year change in total nitrate concentrations at individual measurement locations has been minimal. The ammonium maps for the eastern United States presented in Figure 7-11 shows that the highest ammonium concentrations are also highest in the midwest. This is due to the association of ammonium concentrations to sulfate and nitrate compounds. Although total nitrates have not substantially changed throughout this region, the 10-year decrease in ambient ammonium in the Ohio Valley and elsewhere appears to be associated with the reduction in sulfate concentrations.

Seasonal Trends in SO₂ Emissions and Related Air Quality

Electric utilities account for 70 percent of the SO₂ emissions in the eastern United States and for 75 percent of the 10-year regional reduction in SO₂ emissions. The trend in ambient sulfates and sulfur dioxide are generally consistent with the change in annual sulfur dioxide emissions from electric utilities in the eastern United States. Figure 7-12 shows that the 24-percent 10-year decline in sulfates and 31-percent decrease in ambient SO₂ correspond to the overall 25-percent decline in power plant SO₂ emissions. In addition, the 1998–1999 decrease in ambient rural sulfates (10 percent) and in ambient rural SO₂ (4 percent) appear to follow the 6-percent decrease in annual regional SO₂ power plant emissions.

For annual average ambient sulfur dioxide, the long-term air quality improvement is more substantial and appears similar to the large drop in regional SO₂ power plant emissions which occurred between 1993 and

Figure 7-8. Trend in ambient sulfates in the rural eastern United States, based on CASTNet monitoring data, 1990–1999.

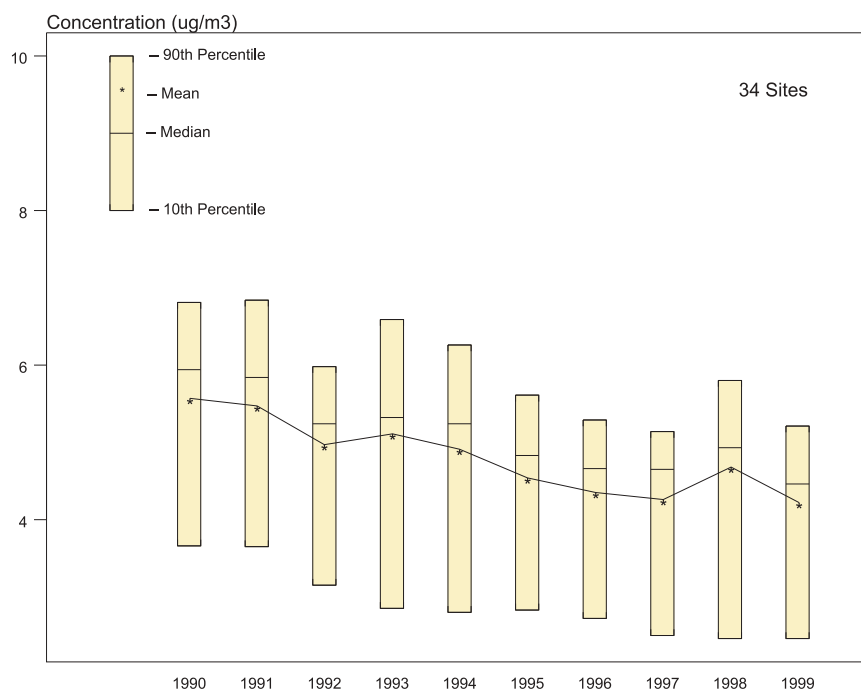


Figure 7-9. Trend in ambient sulfur dioxide in the rural eastern United States, based on CASTNet monitoring data, 1990–1999.

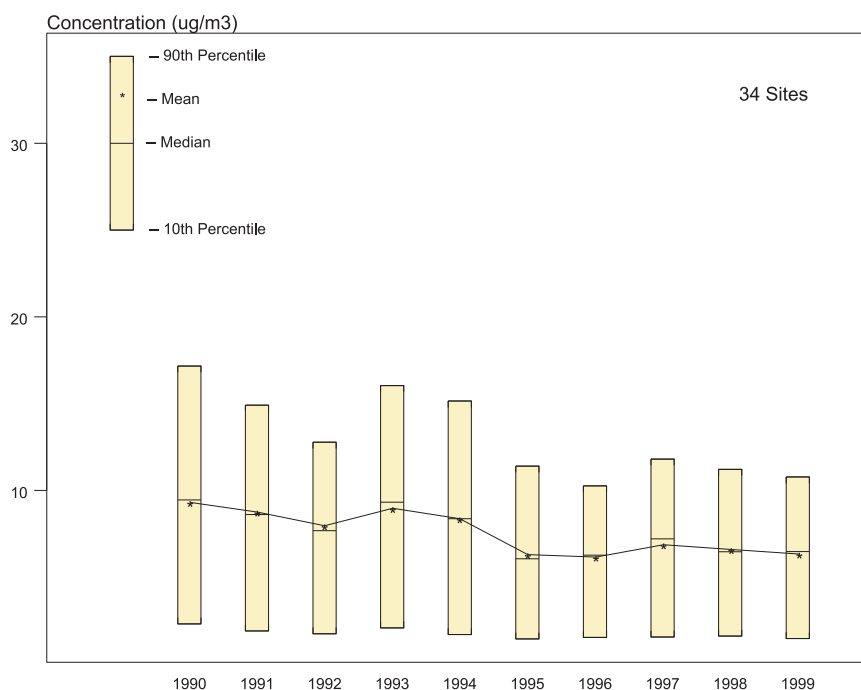
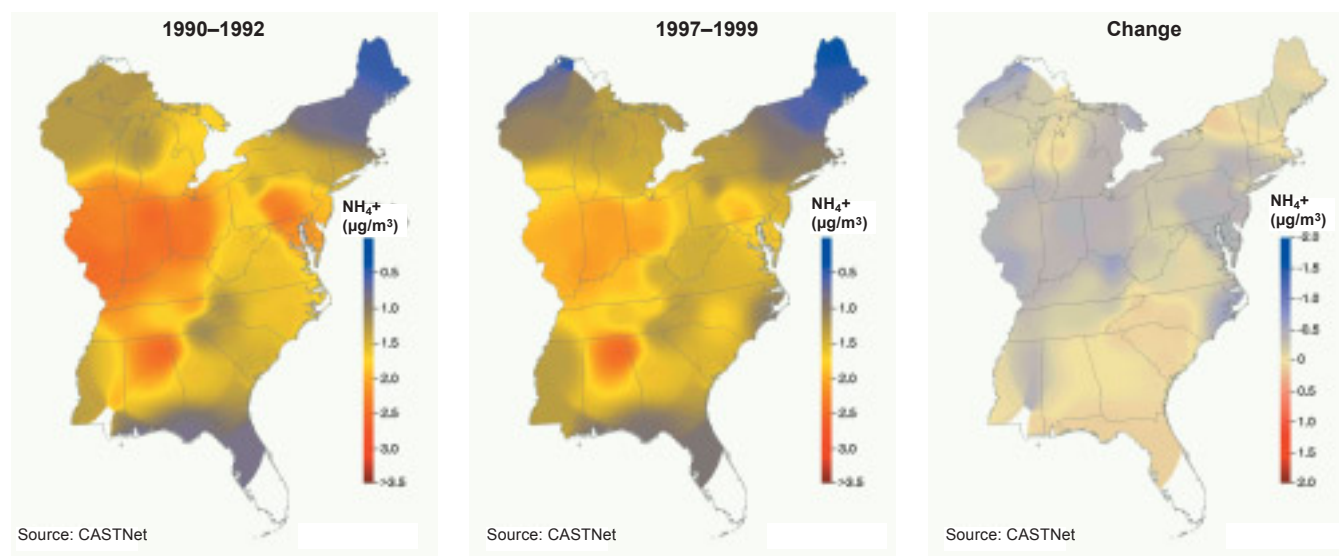
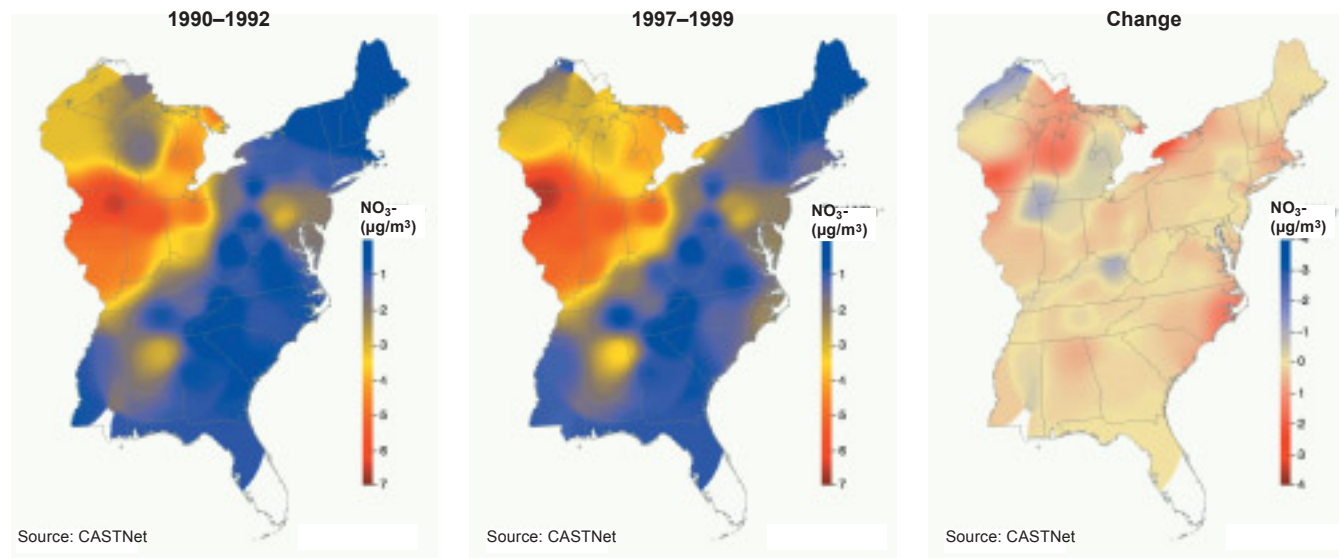


Figure 7-10. Rural annual mean ammonium concentrations from CASTNet, 1990–1992 vs. 1997–1999.**Figure 7-11.** Rural annual mean total nitrate concentrations from CASTNet, 1990–1992 vs. 1997–1999.

1995. For sulfates, the composite average ambient concentrations depict a more gradual change.

Figure 7-13 presents the trends in ambient sulfates, ambient sulfur dioxide, and SO₂ emissions by calendar quarter. The largest 10-year decrease in quarterly average ambient sulfates occurred during the 3rd calendar quarter which is the high sulfate "season." This 3-month period with its slow moving air masses, high photochemical activity and high seasonal SO₂ emissions contributes 65–70 percent to the typical annual average concentrations of sulfates.

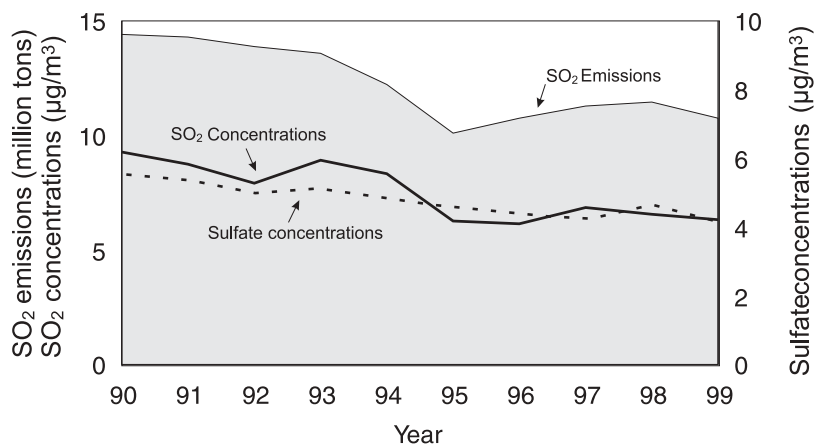
Sulfur dioxide on the other hand depicts its lowest concentration levels during the summer season, but also reveals long term, albeit slightly lower, rural air quality improvement (-25 percent). This contrasts with more significant 10-year changes of -30 percent, -34 percent and -37 percent for the 1st, 2nd, and 4th calendar quarters respectively.

These changes in rural SO₂ match the annual average results presented for urban areas. (See the criteria pollutants section in Chapter 2 for more information about urban ambient SO₂ trends, SO₂ emission trends and the acid rain program. Also see www.epa.gov/airmarkets/.)

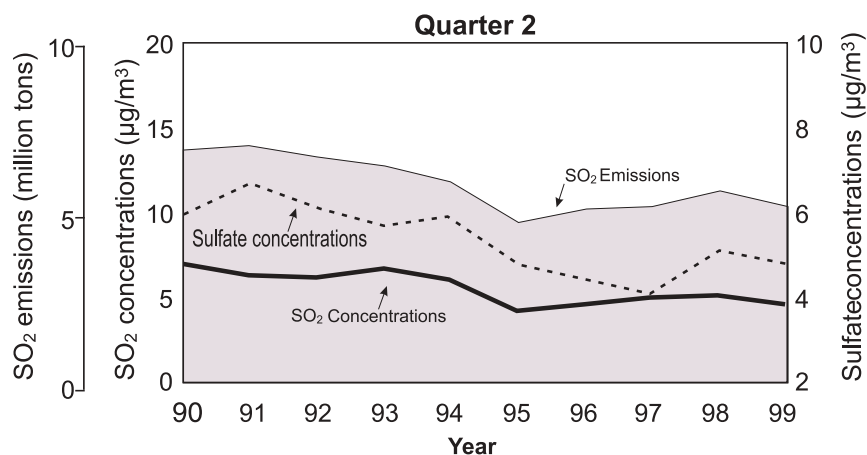
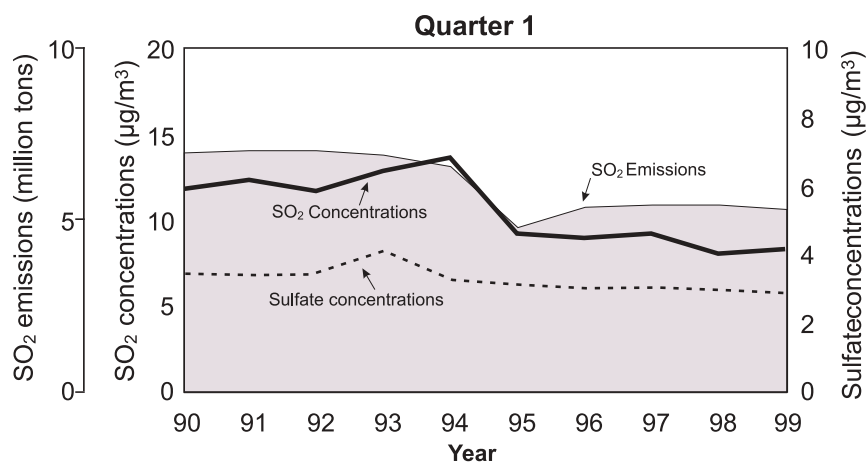
Sulfur and Nitrogen Deposition

Total deposition of sulfur and nitrogen are derived from concentrations of sulfur and nitrogen species in rain combined with estimated deposition resulting from ambient particles and gases. As described for the spatial patterns in measured concentrations of wet and dry sulfur compounds, the highest deposition of sulfur also is estimated to occur in the eastern

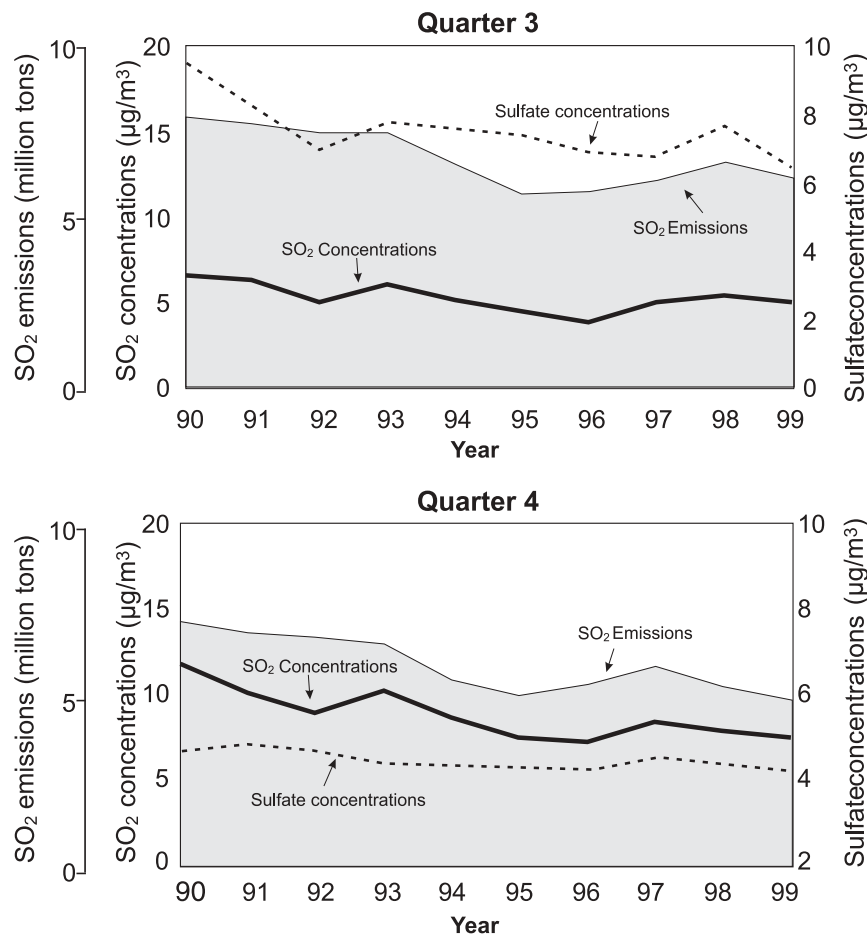
Figure 7-12. Trend in annual mean ambient sulfur dioxide and sulfate concentrations, based on CASTNet monitoring data, and regional SO₂ emissions from electric utilities in rural eastern United States, 1990–1999.



Figures 7-13a. and Figure 7-13b. Trend in annual mean ambient sulfur dioxide and sulfate concentrations, based on CASTNet monitoring data, and regional SO₂ emissions from electric utilities in rural eastern United States by calendar quarter, 1990–1999.



Figures 7-13c. and 7-13d. Trend in annual mean ambient sulfur dioxide and sulfate concentrations, based on CASTNet monitoring data, and regional SO₂ emissions from electric utilities in rural eastern United States by calendar quarter, 1990–1999.



United States. Because of differences in rain, terrain and ground cover there is more spatial variability in estimated deposition than the contributing ambient concentrations. Some of the highest estimated sulfur deposition include areas along and to the East of the Ohio Valley. In these areas, generally at least half (45–65 percent) come from rain. This wet percent ranges from 70–90 percent in the other eastern United States areas with lower sulfur deposition. In all areas of the eastern United States, most of the dry deposition is associ-

ated ambient SO₂ gas. In the West, sulfur deposition is much lower. Most western sulfur is deposited in rain, but the other sulfur is more evenly divided between SO₂ gas and sulfate particle (see Figure 7-14).

Nitrogen deposition comes from ammonium and nitrates in rain and ambient particulate concentrations of those species as well as ambient nitric acid. Based on monitoring stations that provide both wet and dry nitrogen measurements, Figure 7-15 shows that large areas of the eastern United States have similarly high

values of estimated nitrogen deposition. The estimated deposition at western stations is much lower. For eastern stations, 60–70 percent is estimated to come from rain and most of this is associated with ammonium. Almost all of the remaining 30–40 percent is associated with measured nitric acid. In the West, rain accounts for more of the total deposition. Because dry nitrogen measurements are not available for the middle of the country, total nitrogen deposition cannot be estimated for this region. Data from the NADP, however, suggest that high nitrogen deposition would occur in this region. See Figure 7-3 which shows the high deposition of ammonium from precipitation in the region centered on IA.

References

1. Lynch, J.A., J.W. Grim and V.C. Bowersox. 1995. *Trends in Precipitation Chemistry in the United States: A National Perspective, 1980–1992*. Atmospheric Environment Vol 29, No. 11.
2. Lynch, J.A., V.C. Bowersox and J.W. Grim. 1996. *Trends in Precipitation Chemistry in the United States: An Analysis of the Effects in 1995 of Phase I of the Clean Air Act Amendments of 1990, Title IV*. U.S. Geological Survey. Open-file Report 96-0346.
3. Clean Air Status and Trends Network (CASTNet), 1999 Annual Report. <http://www.epa.gov/castnet/reports.html>.

Figure 7-14. Wet and dry components of sulfur deposition, 1999.



Figure 7-15. Wet and dry components of nitrogen deposition, 1999.

